

SUMMARY REPORT

on

CONTINUATION OF THE INVESTIGATION
OF THE REACTION OF TITANIUM
WITH HYDROGEN

to

NASA-MANNED SPACECRAFT CENTER
STRUCTURES AND MECHANICS DIVISION

May 15, 1967

CONTRACT NO. NAS 9-6565

by

B. G. Koehl, W. Hodge, D. N. Williams, and
E. S. Bartlett

BATTELLE MEMORIAL INSTITUTE
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

Battelle Memorial Institute · COLUMBUS LABORATORIES

505 KING AVENUE COLUMBUS, OHIO 43201 · AREA CODE 614, TELEPHONE 299-3151 · CABLE ADDRESS: BATMIN

May 26, 1967

NASA-Manned Spacecraft Center
Structures and Mechanics Division
2101 Webster-Seabrook Road
Houston, Texas 77058

Attention Mr. Sam V. Glorioso/ES
Contract No. NAS 9-6565

Dear Mr. Glorioso:

Thirty copies of a Summary Report on Contract No. NAS 9-6565, "Continuation of the Investigation of the Reaction of Titanium with Hydrogen", are enclosed. This is the number you requested during your recent visit to Battelle. Additional copies, as specified in the contract, are being sent to the General Research Procurement Branch and the Technical Information Dissemination Branch, both at Houston.

Yours very truly,



E. S. Bartlett
Chief
Nonferrous Metallurgy Division

ESB/dc

cc: Mr. H. R. Hodges
Miss Retha Shirkey (4)

TABLE OF CONTENTS

	<u>Page</u>
SUMMARY	1
Stress Studies	1
Pressure Studies	1
INTRODUCTION	2
MATERIALS	3
PHASE 1. STRESSED EXPERIMENTS IN A GLASS SYSTEM	6
Experimental Methods	6
Results and Discussion.	9
PHASE 2. PRESSURE EXPERIMENTS IN THE PRESSURE BALANCE SYSTEM.	14
Experimental Methods	14
Results and Discussion.	19
GENERAL DISCUSSION.	32
FUTURE WORK	33
REFERENCES	33

APPENDIX

EXPERIMENTAL RESULTS	A-1
--------------------------------	-----

LIST OF TABLES

Table 1. Analyses and Mechanical Properties of the Titanium and Titanium Alloy Used in This Work	3
Table 2. Treatments Used to Oxidize Test Samples	4
Table 3. Effect of Stress on the Hydriding Reaction	12
Table 4. Effect of Oxide Film Thickness on Hydriding of Stressed Samples	15
Table 5. Effect of Vacuum Annealing Ti-50A Prior to Exposure to Hydrogen at Greater Than Atmospheric Pressure	20
Table 6. The Effect of the Reaction of Hydrogen on Unabraded Ti-50A Samples at Greater Than Atmospheric Pressures	21

LIST OF TABLES
(Continued)

	<u>Page</u>
Table 7. The Effect of Pressure on the Reaction of Ti-50A With Hydrogen . . .	23
Table 8. The Effect of Exposure to Air After Abrasion and Before Exposure to 311 PSIG (22.1 Atmospheres) Hydrogen for 24 Hours at 99 F . . .	25
Table 9. The Effect of a Static Stress Near the Yield Stress on the Reaction of Titanium with 312 PSIG (22.2 Atmospheres) Hydrogen for 24 Hours at 99 F	28

LIST OF FIGURES

Figure 1. Microstructures of the Four Titanium Materials.	5
Figure 2. Diagram of Glass System	7
Figure 3. Full-Scale Sketch of Sample Holder for Applying Stress	8
Figure 4. Sketch of the Method for Applying Stress to the Sample	10
Figure 5. Method of Producing Stress in Titanium Sample in Glass System . . .	11
Figure 6. Sample 16-S Acicular Ti-6Al-4V Showing Result of Hydriding Under Stress for 138 Hours at 80 F	13
Figure 7. Diagram of Quartz-Spring Pressure Balance	16
Figure 8. The Quartz-Spring Pressure Balance System	17
Figure 9. The Effect of Hydrogen Pressure on Hydride-Layer Thickness . . .	24
Figure 10. The Effect of Exposure to Air After Abrading and Prior to Exposure to Hydrogen	26
Figure 11. Hydride on Stressed Area of Acicular Ti-50A Sample	29
Figure 12. Hydride on Equiaxed Ti-50A Sample	29
Figure 13. Hydride Areas on Inside of Titanium Tubing Sample 27	30
Figure 14. Surface of Inside of Titanium Tubing Which Was Etched and Did Not Hydride, Sample 28	30
Figure 15. Hydrided Area on Inside of Titanium Tubing Sample 29	31
Figure 16. A Representative Area of Hydride Formed on Inside of Titanium Tubing Sample 29	31

CONTINUATION OF THE INVESTIGATION OF THE REACTION OF TITANIUM WITH HYDROGEN

by

B. G. Koehl, W. Hodge, D. N. Williams, and
E. S. Bartlett

SUMMARY

This investigation continues the work begun under Contract No. NAS 9-5298 and reported July 14, 1966.* This previous work was concerned with determining whether titanium and titanium alloys could be made to react consistently with hydrogen at low temperatures and low to medium pressures. The continuation of this work was undertaken in two phases characterized as follows: (1) the effect of stress on the titanium-hydrogen reaction at low temperatures and 1 atmosphere pressure of hydrogen and (2) the significance of the hydrogen pressure, surface cleanliness, and microstructure on the titanium-hydrogen reaction at hydrogen pressures above atmospheric. From this work it was hoped that a method of suppressing the titanium-hydrogen reaction could be found.

Stress Studies

Twenty-six experimental runs were made at 80 to 140F with Ti-50A and Ti-6Al-4V specimens exposed to hydrogen at atmospheric pressure. These specimens were stressed by bending over a mandrel by the oscillation of large magnets outside the reaction tube. No reaction occurred with any abraded and stressed Ti-50A specimens, which had not been previously vacuum annealed to clean the surface, even though some of the samples failed by fatigue. One specimen of Ti-6Al-4V reacted. A reaction could not be initiated by stress that cracked the outer oxide layer and apparently did not crack an inner bronze-colored oxide layer on specimens which had been deliberately oxidized to form a heavy, and presumably more brittle, oxide layer on the sample surface.

Pressure Studies

A quartz-spring pressure balance was used to investigate:

- (1) The effect of hydrogen pressure on the titanium-hydrogen reaction. It was found that abraded but unannealed Ti-50A specimens reacted with hydrogen throughout a pressure range of 2 psig (1.1 atmospheres) to 1005 psig (69.5 atmospheres). Because of instability in the pressure balance no reaction rate vs pressure data could be obtained; however, a definite correlation was obtained between hydrogen pressure and hydride-layer thickness.

*References are given on page 33.

- (2) The effect of microstructure on the titanium-hydrogen reaction. The acicular structure proved to be the most reactive of three Ti-50A structures - acicular, cold rolled, and equiaxed. Cold-rolled and equiaxed materials were about equal in reactivity. In samples which were surface abraded and exposed to air for varying lengths of time before hydrogen exposure, the hydriding reaction was retarded the least for the acicular material and the most for the equiaxed material.
- (3) The effect of stress on the titanium-hydrogen reaction at hydrogen pressures above 1 atmosphere. No effect of static stress near the yield stress was noted at 312 psig (22.2 atmospheres) hydrogen pressure.
- (4) The hydriding of the Beech Aircraft titanium tubing. It was found that hydriding occurred at 99 F and 315 psig (22.4 atmospheres) hydrogen pressure on the inside of the material in the as-received condition. This reaction was prevented by etching in HNO_3 -HF- H_2O solution and increased by rubbing the inside with high-carbon, high-chromium steel.

It is believed that the tubing is being activated by the rubbing or scratching of the inside of the tubing on a mandrel during fabrication. Elimination of this abrasion of the inside of the tube would help prevent the hydriding reaction from taking place. If this is not possible, a thorough etching of the tubing after fabrication should remove the scratches or the activating agent. As a final precaution, heating in air of the final assembly would produce an oxide layer over the surface which would minimize attack by the hydrogen.

INTRODUCTION

A research program entitled "An Investigation of the Reaction of Titanium with Hydrogen" was conducted at Battelle during the period October 19, 1965, through June 18, 1966, under Contract No. NAS 9-5298.(1) This program was initiated as the result of an unexpected failure observed in liquid-hydrogen storage tanks of the type used to supply fuel cells for spacecraft.(2) Erosion of the inside surface of certain titanium tank components exposed to gaseous hydrogen at moderate pressure was observed during preliminary testing and found to result from hydride formation.

During the research conducted under Contract No. NAS 9-5298 it was found possible to cause a reaction to occur between unalloyed titanium and hydrogen at room temperature and 1 atmosphere pressure. A clean, oxide-free, titanium surface and hydrogen gas of the highest purity were absolutely essential to insure a reaction.

Factors that assisted in promoting a reaction but were not essential were a large titanium surface area, an acicular microstructure, and galling of the titanium surface with iron.

Despite the fact that a surface hydriding reaction was observed in these studies, the conditions necessary for its occurrence in the laboratory were much more restrictive than anticipated. It seemed unlikely that similar conditions would have been developed in the liquid-hydrogen tank which had failed during the preliminary test program.

Surface cleanliness and hydrogen purity were not obtainable at greater than atmospheric pressures in the equipment available for this work, nor could any form of stress be applied to the specimen. Both of these factors may have contributed to the tank failure. Therefore, it was considered essential to continue the studies to determine the importance of stress and pressures above 1 atmosphere on the reaction of titanium with hydrogen.

MATERIALS

Unalloyed titanium (Ti-50A) and Ti-6Al-4V sheet were obtained from Titanium Metals Corporation of America (TMCA). The chemical analyses and mechanical properties of these materials are given in Table 1.

TABLE 1. ANALYSES AND MECHANICAL PROPERTIES OF THE TITANIUM AND TITANIUM ALLOY USED IN THIS WORK

<u>Chemical Analyses of Alloys as Received, percent by weight(a)</u>							
<u>Alloy</u>	<u>C</u>	<u>Fe</u>	<u>N</u>	<u>Al</u>	<u>V</u>	<u>H</u>	<u>O</u>
Ti-50A	0.023	0.10	0.012	--	--	0.003	0.11(b)
Ti-6Al-4V							
ELI	0.023	0.12	0.013	5.9	3.9	0.007	0.08(b)
<u>Mechanical Properties of Alloys as Received(a)</u>							
<u>Alloy</u>	<u>Yield Strength,</u> <u>psi</u>	<u>Tensile Strength,</u> <u>psi</u>	<u>Elongation,</u> <u>percent</u>	<u>Bend</u> <u>Test</u>	<u>Gage,</u> <u>in.</u>		
Ti-50A L(c)	53,500	66,100	29.0	1.5	0.032		
Ti-6Al-4V							
ELI L	133,800	142,400	12.0	4.0	0.036		
T	134,600	140,200	14.0	4.0			

(a) Data furnished by TMCA, except as noted.

(b) Battelle analysis.

(c) L = longitudinal to the rolling direction, T = transverse to the rolling direction.

The Ti-50A and Ti-6Al-4V used in this program were cold rolled to 15-mil thickness from the original thickness of 32 and 36 mils, respectively. The cold-rolled strip was then heat treated as follows:

Ti-50A

- (1) No heat treatment, specimen was cold rolled 53 percent.
- (2) Annealed for 1/2 hour at 1750 F in argon and slow cooled to produce a coarse acicular alpha microstructure.
- (3) Annealed for 1/2 hour at 1200 F in argon and air cooled to produce a fine-grained equiaxed alpha microstructure.

Ti-6Al-4V

- (1) Annealed for 1/2 hour at 1750 F in argon and slow cooled to produce a coarse acicular alpha microstructure.

These treatments provided four different materials for evaluation. The resulting microstructures are shown in Figure 1. Of particular interest are the observations that a significant amount of beta was present in the acicular Ti-50A and that the acicular Ti-6Al-4V developed a considerably finer structure than the acicular Ti-50A.

Some of the material was exposed to air for varying lengths of time and at various temperatures to produce surface oxide layers in a range of thicknesses. The treatments used and the oxide thicknesses produced are shown in Table 2.

TABLE 2. TREATMENTS USED TO OXIDIZE TEST SAMPLES

Oxidation Treatment		Weight Gain, gm/sq in.	Calculated Oxide Thickness, microinches ^(a)
Time, hours	Temperature, F		
6	1150	0.00079	11
6	1150	0.00081	12
6	1150	0.00102	15
10	1150	0.00142	20
10	1150	0.00151	22
15	1150	0.00197	28
36	1150	0.00400	57
1	1450	0.00521	75
5 minutes	1800	0.01041	149

(a) Calculation method:

$$\text{Oxide film thickness in microinches} = \frac{\text{Weight gain in grams}}{\text{Surface area (in.}^2\text{) of sample}} \times \frac{1}{69.82}$$

This assumes that: All oxygen absorbed is utilized in forming oxide.
Oxide is rutile TiO_2 with density of 69.82 g/in.³.

- a. Ti-50A
Coarse acicular
structure



250X

8B552

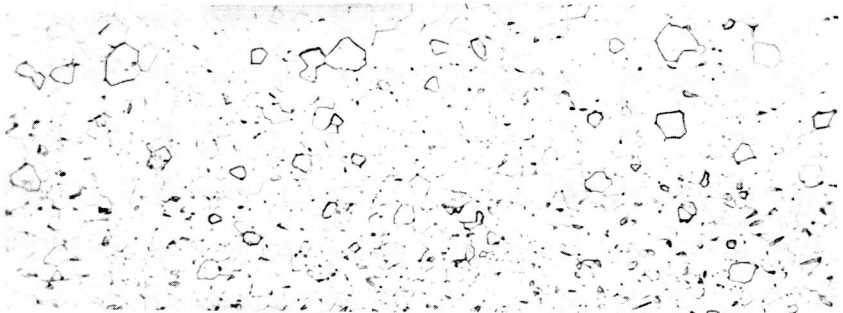
- b. Ti-50A
Cold-rolled
structure



250X

8B553

- c. Ti-50A
Fine equiaxed
structure



250X

8B554

- d. Ti-6Al-4V
Coarse acicular
structure



250X

8B555

FIGURE 1. MICROSTRUCTURES OF THE FOUR TITANIUM MATERIALS

A short length of Ti-55A titanium tubing (7-mm OD, 5-1/2-mm ID) was obtained from Beech Aircraft. This was from the same lot of material used in the lines of a liquid-hydrogen tank which hydrided. The material, which was supplied in the "as-received" condition, had an equiaxed alpha microstructure.

Hydrogen gas was obtained from the Matheson Company. Ultrapure-grade hydrogen with a dew point of lower than -80 F and impurities of <1 ppm O₂, <5 ppm N₂, and <1 ppm total hydrocarbons (as CH₄) was used in all of this program.

PHASE 1. STRESSED EXPERIMENTS IN A GLASS SYSTEM

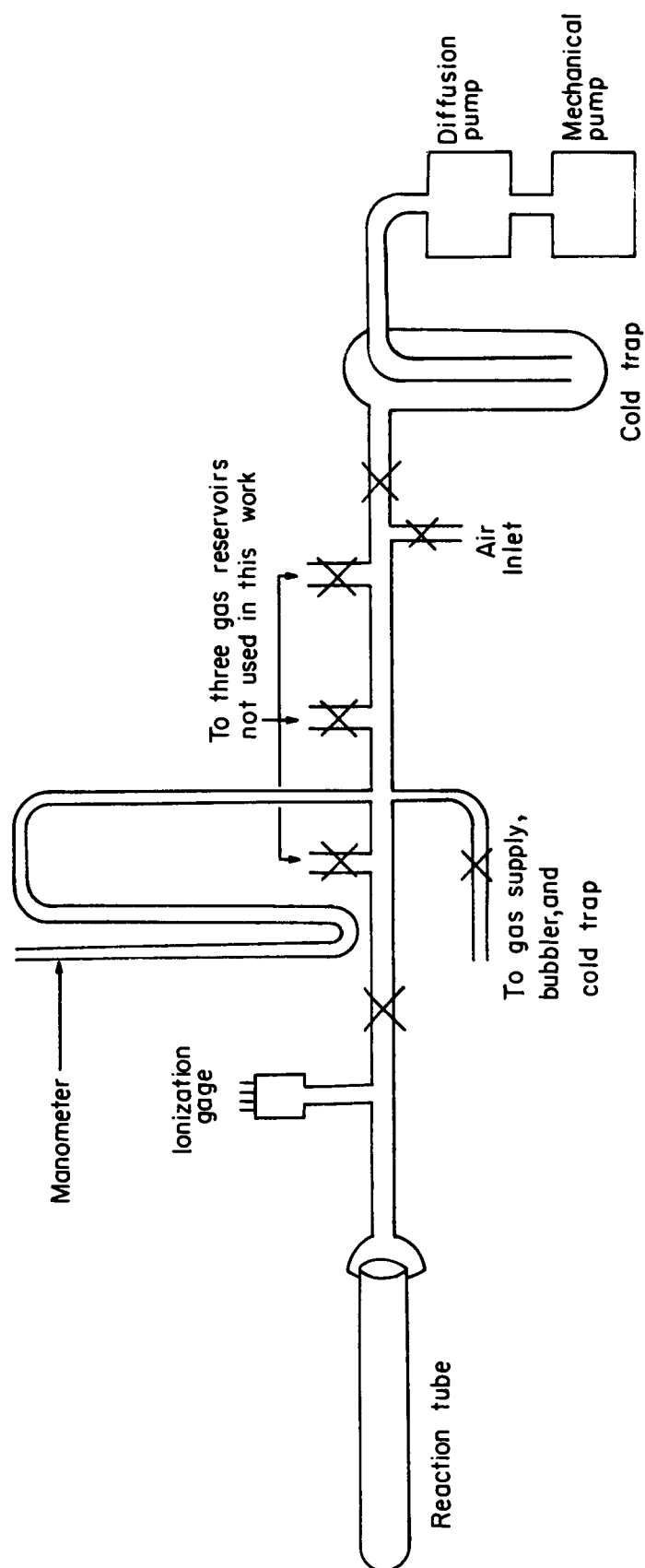
Experimental Methods

The glass system employed in the previous work under Contract No. NAS 9-5298(1) was used to study the effect of stress on the reaction of titanium with hydrogen at atmospheric pressure. The system is shown schematically in Figure 2. The glass system consisted of a mechanical pump, glass mercury diffusion pump, and a cold trap, which together made up the pumping system. The three large gas-storage reservoirs attached to the main pump-out line were not used in this work and were closed-off by means of large stopcocks. A full-length open-end mercury manometer was connected in the pump-out line and was used to measure pressure change during the experiments. Knowing the calibrated volume of the system (1309 ml STP) and the pressure change, the quantity of hydrogen absorbed during an experimental run was easily calculated. An ionization gage was used to monitor the system during evacuation and annealing. The reaction tube was constructed of 46-mm ID Vycor and was 25 inches in length. The foil or samples were heated by a resistance-wound furnace that was monitored by a Foxboro Controller. The main pump-out line was constructed of 12-mm Pyrex tubing, except for the section just preceding the reaction tube which was 25-mm ID. Hydrogen was admitted to the system after first passing through a mercury safety bubbler and a liquid-nitrogen cold trap.

The samples were 3/4 inch wide, 3 inches long, and 15 mil thick and were abraded with dry 240-grit silicon carbide paper and rinsed in cp acetone before bolting into the sample holder.

The sample holder was constructed of Type 304 stainless steel and consisted of two identical sections. When assembled, with the sample bolted between the sections, the holder was 5 inches in length by 1-1/4 inches square. A drawing of the sample holder is shown in Figure 3. Two sample holders were constructed. One sample holder was machined to a 2.54-inch radius. This provided a maximum strain in 15-mil-thick sheet of 0.3 percent equivalent to a stress of about 50,000 psi assuming elastic binding. The second sample holder was machined to a 0.75-inch radius to provide a maximum fiber strain of 1.0 percent, which would provide appreciable plastic flow on the sample surface.

The holder containing the sample was placed inside the Vycor reaction tube which was immediately sealed to the vacuum system and evacuated. The evacuation was continued with numerous periods of flaming the glassware until the system pressure was



A-53865

FIGURE 2. DIAGRAM OF GLASS SYSTEM

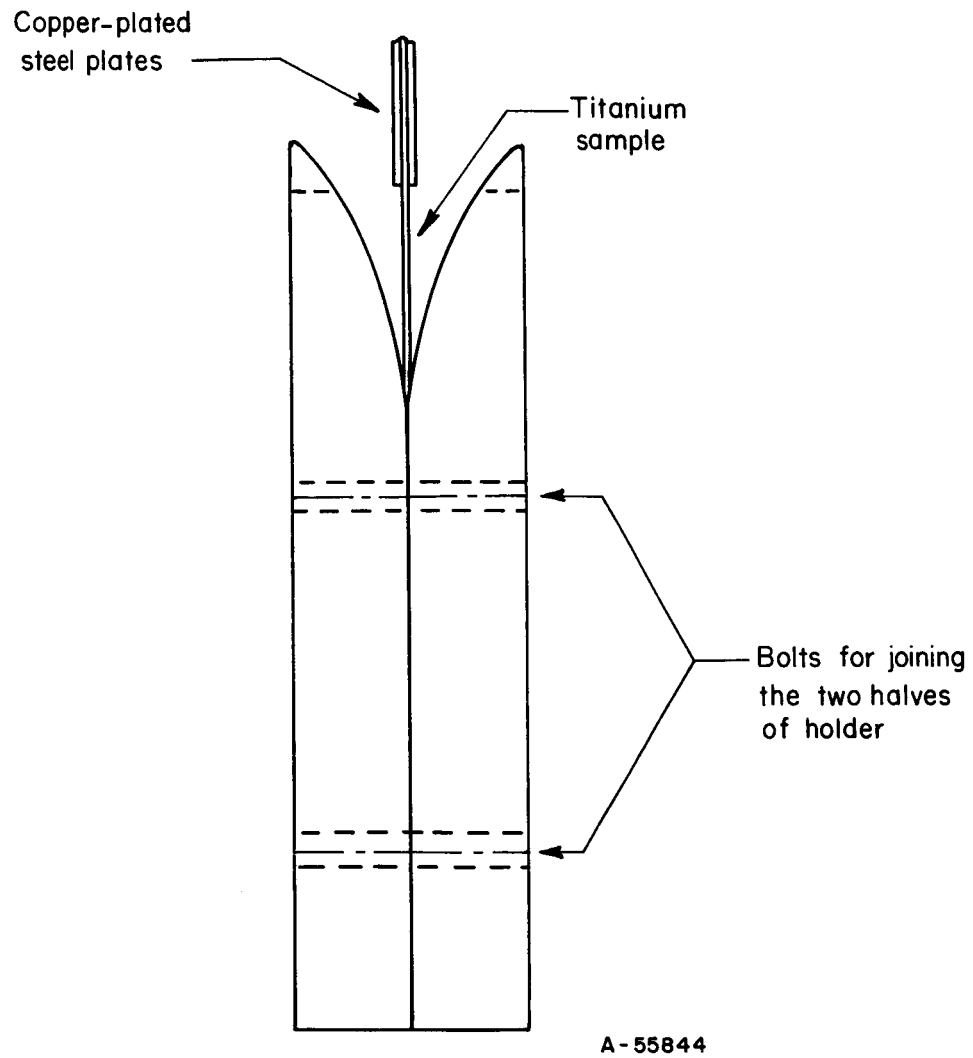


FIGURE 3. FULL-SCALE SKETCH OF SAMPLE HOLDER
FOR APPLYING STRESS

0.05 micron or lower. This required about 1 to 2 hours depending on conditions. The leak rate, or increase in pressure when the reaction system was isolated from the pumps, was highly important in this work to prevent the samples from becoming contaminated. A period of about 4 minutes of isolation occurred during each run while the hydrogen was being flushed through the remainder of the system to be certain that no air was present in the lines. This leak rate averaged about 0.02 micron/minute for all the experimental runs. This rate agreed with that found in the previous work on Contract No. NAS 9-5298.⁽¹⁾ Since reaction of the titanium with hydrogen was not prohibited by a leak rate of such a magnitude in that work, it was believed to be of a safe level for this work also.

When the system pressure was reduced to about 0.05 micron and the leak rate became correspondingly low, the samples or foil were heated to 1500 F and held for 2 hours, then cooled to room temperature in a dynamic vacuum. In the majority of experimental runs 90 square inches of unabraded Ti-65A 2-mil foil was heated in this manner while the sample in another part of the reaction tube was not heated. It had been found in previous work⁽¹⁾ that titanium foil which had been activated by annealing acted as a getter and helped to insure a reaction between hydrogen and the titanium sample. The reaction system was then isolated for approximately 4 minutes while the gas inlet lines were flushed; then ultrapure hydrogen, dried by passing through a liquid nitrogen cold trap, was added to bring the system to atmospheric pressure. This addition normally took about 30 minutes at a rate of about 45 ml/min.

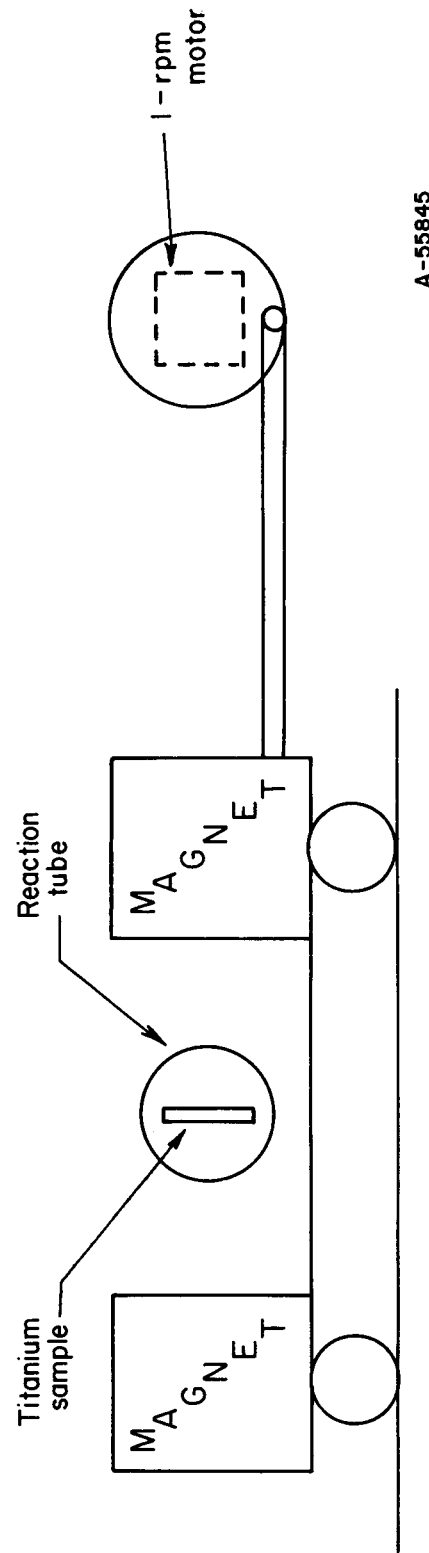
Flexing, to stress the sample, was begun immediately after addition of the hydrogen. This was produced by an externally applied magnetic force consisting of two large permanent horseshoe magnets mounted on a moveable platform as shown in Figures 4 and 5. A 1 rpm electric motor oscillated this platform first in one direction then the other, resulting in one complete cycle of strain (maximum tension through maximum compression and return) per minute. Because titanium is nonmagnetic, small copper-plated steel plates were bolted to both sides of the sample at the end which was free to flex. All experimental runs were made at room temperature, about 80 F, unless otherwise noted. Heating tape wound on the outside of the reaction tube provided the heat for the experimental runs made above room temperature.

After removal from the reaction tube, the samples were sectioned longitudinally, mounted, polished, and etched for microscopic examination of any hydride layer present.

A summary of all experimental work in this equipment is given in the Appendix, Table A-1.

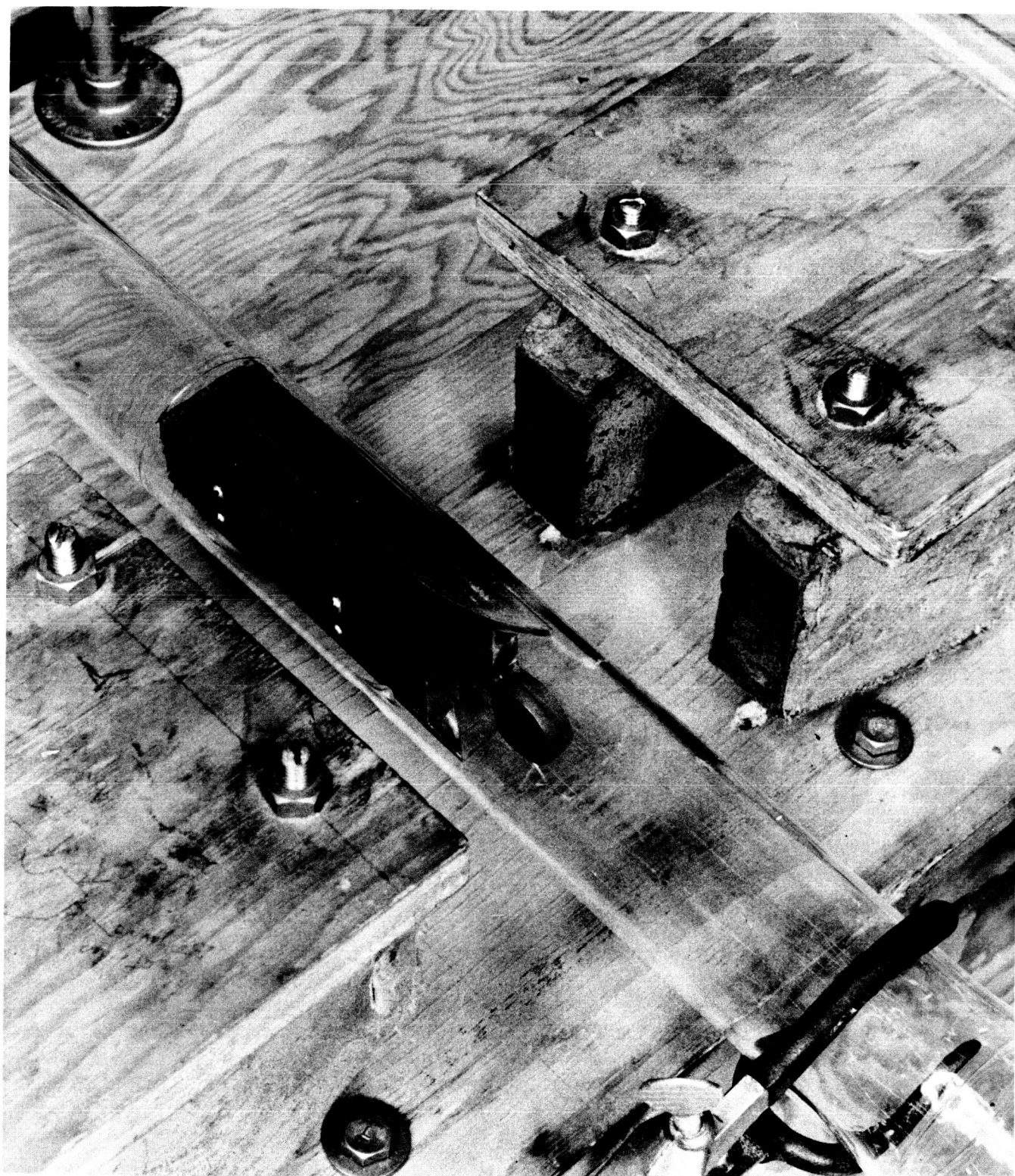
Results and Discussion

It was found in initial work⁽¹⁾ that a titanium-hydrogen reaction would take place if the unstressed sample had been previously vacuum annealed to dissolve the surface oxide. Three experimental runs were made to confirm this conclusion, to check the modified equipment for cleanliness, and to ascertain whether the sample holder, by its presence in the system, would prevent hydriding of the sample. Results are listed in Table 3. Hydriding of the Ti-50A took place in all three cases but, as indicated in



A-55845

FIGURE 4. SKETCH OF METHOD FOR APPLYING STRESS TO THE SAMPLE



37480

FIGURE 5. METHOD OF PRODUCING STRESS IN TITANIUM SAMPLE
IN GLASS SYSTEM

Sample is shown bolted in holder inside the Vycor reaction
tube positioned between the two oscillating magnets. This
was part of the glass vacuum system.

BATTELLE MEMORIAL INSTITUTE

TABLE 3. EFFECT OF STRESS ON THE HYDRIDING REACTION

Maximum Outer Fiber Strain, %	Test Temperature, F	Sample Vacuum Annealed	Hydriding Observed	Sample Nos. (a)
<u>Acicular Ti-50A</u>				
0	80	Yes	Yes	TR-1, TR-2, TR-3
0	80	No	No	TR-4
0.3	80	Yes	Yes	2-S
0.3	80	No	No	1-S, 3-S, 5-S, 11-S, 12-S, 18-S, 19-S
0.3	250	No	No	13-S
1.0	80	No	No	22-S, 27-S
1.0	80 α 170 (b)	No	No	24-S
<u>Acicular Ti-6Al-4V</u>				
0.3	80	No	Probable ^(c)	16-S, 17-S
1.0	80	No	No	25-S

(a) Complete data given in Appendix, Table A-1.

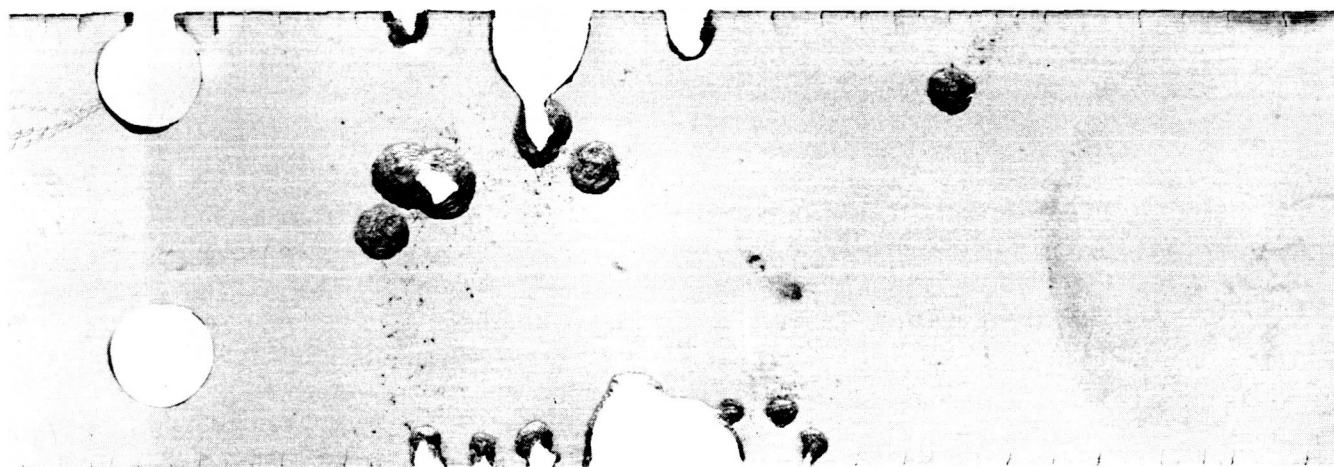
(b) Sample first stressed 89 hours at 80 F, then an additional 27 hours at 170 F.

(c) One sample reacted extensively, one did not. Sample which reacted had foil getter in reaction chamber.

Table 3, did not when a fourth sample was exposed to hydrogen without vacuum annealing. These results were as expected from the experience of the previous work.

The effect of stress on the reaction of Ti-50A and Ti-6Al-4V with 1 atmosphere of hydrogen is given in Table 3. It can be seen that no hydriding reaction occurred with any nonvacuum-annealed Ti-50A sample under a maximum outer fiber strain of 0.3 percent at 80 F. Increasing the temperature to 250 F did not initiate a reaction. The only sample which reacted (2-S) did so after a vacuum anneal to dissolve the surface oxide prior to hydrogen exposure. A very small spot of hydride was found on Sample 1-S. This probably resulted from a scratch on the surface and was not of sufficient size to record as a reacted sample. Increasing the maximum outer fiber strain to 1 percent did not result in any hydriding reaction at temperatures to 170 F even though several samples broke in fatigue from the effect of the strain.

As indicated in Table 3, two experimental runs were made using samples of Ti-6Al-4V at the low strain level at 80 F. One nonvacuum-annealed sample (16-S) reacted extensively as shown in Figure 6, the other did not. A third sample strained 1 percent at 80 F did not react. A Ti-65A, 2-mil foil (90 square inches) was present as a getter in the reaction tube with the sample which reacted. Although the titanium foil appeared to have been effective in helping to initiate a reaction with Sample 16-S, its presence in the Ti-50A runs did not appear to aid in obtaining a hydriding reaction.



3X

4B106

FIGURE 6. SAMPLE 16-S ACICULAR Ti-6AL-4V SHOWING RESULT OF HYDRIDING UNDER STRESS FOR 138 HOURS AT 80 F

Hydriding is concentrated in the most highly stressed area.
Note: Smooth holes at one end were used to secure sample in holder.

The effect of the oxide film thickness on the reaction of stressed samples with 1 atmosphere hydrogen pressure is shown in Table 4. Experimental runs were made with samples having oxide film thicknesses ranging from 11 to 145 microinches and with both acicular and equiaxed structures. Maximum outer fiber strain of 0.3 and 1.0 percent applied at temperatures from 80 to 140 F did not initiate a hydriding reaction in any sample.

The samples having the thickest oxide layer, 75 and 149 microinches, showed a definite cracking of the gray-white outer layer under the effect of strain, but no rupture of the inner bronze-colored oxide layer was apparent. The outer oxide layer did not crack on layers less than 75 microinches in thickness.

PHASE 2. PRESSURE EXPERIMENTS IN THE PRESSURE BALANCE SYSTEM

Experimental Methods

A newly constructed quartz-spring pressure balance was used to study the effect of pressure on the reaction of titanium with hydrogen. This equipment is shown in Figures 7 and 8.

The balance can be divided into two sections, the upper or suspension section and the lower reaction section. All sections were made of stainless steel and were bolted together with stainless steel flanges using O rings as pressure and vacuum seals.

The reaction section consisted of a resistance-wound (McDaniel) impervious ceramic tube of 1-inch ID and 12 inches in length. Three individually wound furnace sections had separate thermocouples and Variac Controls; the center section was monitored by a Foxboro controller. The heating elements were surrounded by a spiral of molybdenum sheet which acted as a radiation shield. All wires and tubing for evacuating and admitting gas were brought in through the bottom stainless steel plate. The outside of the reaction section and the narrow section of stainless steel tube between this section and the cathetometer viewing port were incased in copper tubing for water cooling or warming as desired.

The upper suspension section contained a stainless steel housing for a windlass from which a gold chain was suspended. The quartz spring was suspended from this chain. A 0.004-inch-diameter molybdenum wire was, in turn, suspended from the quartz spring. The sample was fastened to this wire by a small Vycor hook. All samples were 2 inches long, 1/2 inch wide, and 15 mils thick, and unless otherwise stated, were dry abraded with 240-grit silicon carbide paper and rinsed in cp acetone before suspending in the pressure balance system.

The suspension wire was lowered through the access port in the bottom of the reaction section by turning the windlass, and a sample was fastened to this wire through a hole bored in one end of the sample. The sample was then raised to the center of the furnace tube by the windlass and the entire system evacuated overnight by a Welch Duo-Seal mechanical pump and an oil diffusion pump. Circulating hot water in the coils on

TABLE 4. EFFECT OF OXIDE FILM THICKNESS ON HYDRIDING OF STRESSED SAMPLES

Oxide Film Thickness, μin	Maximum Outer Fiber Strength, %	Test Temp, F	Hydriding	Sample Nos. (a)
<u>Acicular Ti-50A</u>				
15	0.3	80	No	6-0-S
22	0.3	80	No	7-0-S
28	0.3	80	No	8-0-S
75	0.3	80	No	15-0-S
20	0.3	140	No	10-0-S
75	0.3	80 α 140(b)	No	14-0-S
57	1.0	80 α 140(b)	No	26-0-S
75	1.0	80 α 140(b)	No	20-0-S
149	1.0	80 α 140(b)	No	21-0-S
<u>Equiaxed Ti-50A</u>				
12	0.3	80 α 140(b)	No	9-0-S
11	1.0	80	No	23-0-S

(a) Complete data given in the Appendix, Table A-1.

(b) Samples stressed for varying times at 80 F before increasing temperature to 140 F.

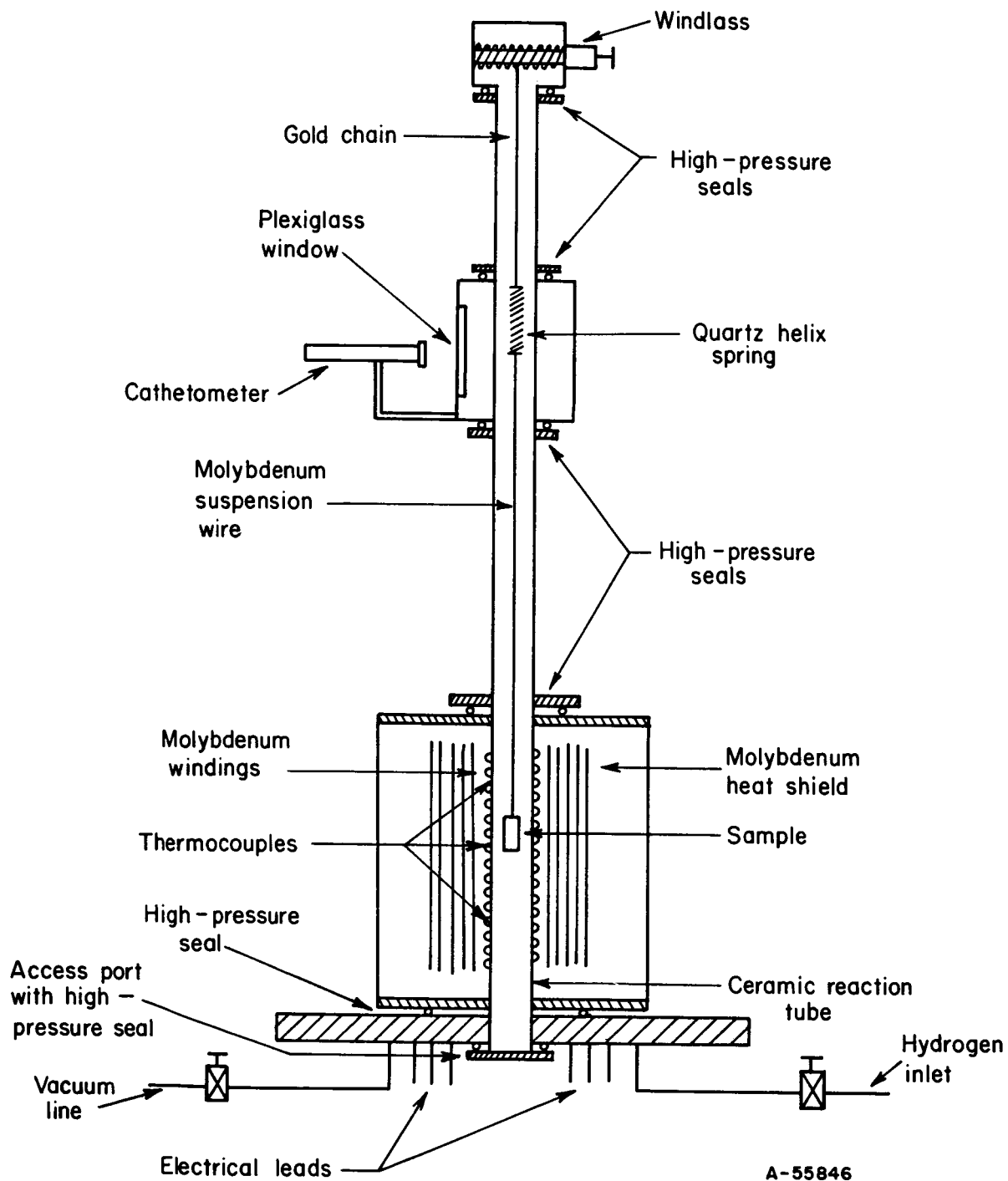
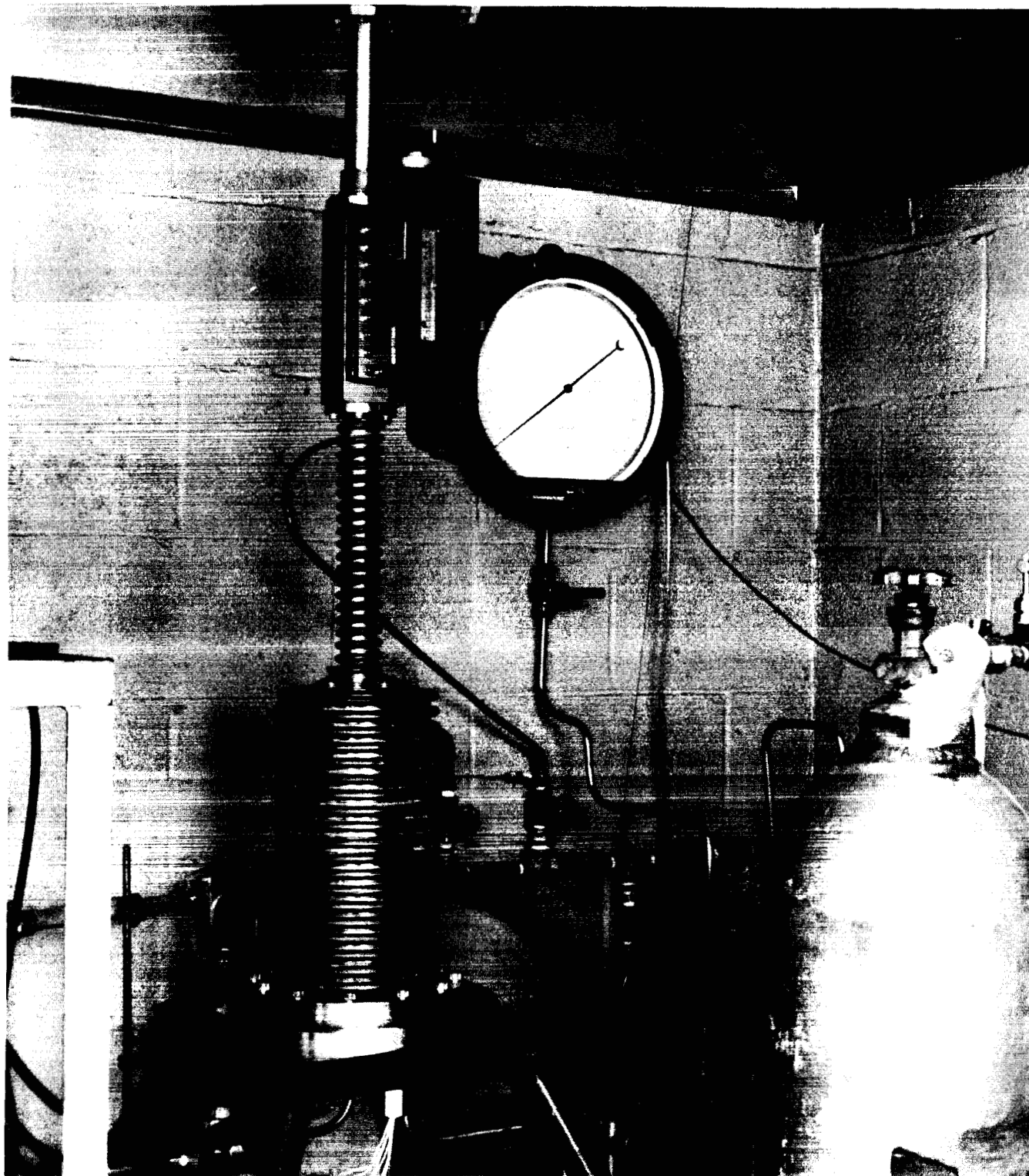


FIGURE 7. DIAGRAM OF QUARTZ-SPRING PRESSURE BALANCE



37481

FIGURE 8. THE QUARTZ-SPRING PRESSURE BALANCE SYSTEM

the outside of the reaction chamber and the section just above it warmed the system sufficiently to insure obtaining a good vacuum. A system pressure of the order of 0.02 to 0.03 microns was consistently obtained after an overnight evacuation. This pressure was read on the 3/8-inch ID pump-out line by a Consolidated Electrodynamics Discharge Gage outside the reaction system. A more accurate reading of the pressure could have been obtained with a gage located inside the reaction section; however, the high pressure which must be sustained in this area made this impractical.

Ultra-pure hydrogen was passed through a liquid-nitrogen cold trap before being admitted to the system at the rate of about 30 psig/min. The gas inlet line was 1/4-inch pressure tubing with Ermeto fittings and Autoclave pressure valves. The pressure was read on a 10-inch Heise Bourdon gage with readings accurate to 1 psig.

The weight change of the sample was read by measuring the change in length of the quartz spring with a cathetometer. This sighting was made through a Plexiglass insert in the side of the upper tube, using the lower hook of the quartz spring as a reference point. Calibration of the quartz spring with known weights gave a value of 0.00026-gram weight change for every 0.001-inch change in spring length.

It was soon found that a discrepancy existed between the weight gain of a sample as calculated from spring change and that found from weighings made of the sample on an analytical balance before and after reacting with hydrogen. After an extensive investigation it was discovered that slight temperature changes both inside and outside the system were causing expansion and contraction of the metal housing of the balance. This slight movement was greatly magnified by the cathetometer and accounted for the discrepancies.

Since neither sufficient time nor funds were available to correct this trouble, it was decided to continue using the system but to discontinue the use of the quartz spring; consequently, no reliable rate data could be obtained. A number of attempts were made to calculate a correction factor to apply to the rate data that had been obtained; however, because of the many variables involved, none could be found that would satisfy the conditions in all cases.

The effect of exposure of the titanium specimens to air for varying periods of time after abrading and prior to exposure to hydrogen was investigated using the reaction section of the pressure balance. Five titanium samples, each 2 inches x 1/2 inch x 15 mils, were dry abraded with 240-grit silicon carbide paper, rinsed in cp acetone, and exposed to air for 5 minutes, 15 minutes, 1 hour, 2 hours, and 4 hours, respectively. They were then suspended in the center of the reaction tube by a wire stand whose base rested on the cover of the access port at the lower end of the reaction tube. After the usual overnight evacuation the samples were exposed to 300 psig (21.4 atmospheres) hydrogen pressure at 99 F for 24 hours. They were then prepared for metallographic examination. Acicular, equiaxed, and cold-rolled Ti-50A and the acicular Ti-6Al-4V were exposed in this manner.

The effect of a static stress on the reaction of titanium with 300 psig (21.4 atmospheres) of hydrogen at 99 F for 24 hours was studied. The same suspension system used in the previous study was used in this series of experimental runs.

To produce a stress just above the yield point the samples measuring 1-1/4 inches x 1/2 inch x 15 mils were bent over a 1/16-inch die in the center of the 1-1/4-inch length. A stainless steel bolt was placed through the two legs of the bent samples and tightened until the legs no longer returned to their original position when the stress was removed. Trial bending and stressing of each material, (acicular, equiaxed, and cold-rolled Ti-50A and acicular Ti-6Al-4V,) to determine the proper bolt adjustment was made prior to the preparation of the specimens for the actual experimental run to predetermine the exact amount of stress necessary to just exceed the yield point of each material. One group of samples of each material was abraded with dry 240-grit silicon carbide paper, rinsed in cp acetone, and bent and stressed. Total time in air after abrasion was 5 to 10 minutes. A second group of the same four materials was stressed but not abraded, only degreased, before the run was made. A third group of the four materials was abraded, bent, and stressed, then reabraded along the stressed area, degreased, and immediately sealed in the reaction system and evacuated. To minimize exposure to air the samples were not weighed. After exposure to hydrogen the specimens were prepared for metallographic examination.

The short length of Ti-55A titanium tubing (7-mm OD, 5-1/2-mm ID) obtained from Beech Aircraft provided the material for four experimental runs. Three of the runs, using 37-mm-long sections of the tubing were made by suspending the samples from the quartz spring of the balance. The fourth run on a 12-mm-long sample was made with the sample suspended from the wire stand described previously. The three larger samples were reacted in the as-received condition, etched with H₂O-HNO₃-HF solution, and rubbed on the inside only with high-carbon, high-chromium steel, respectively. The small sample was rubbed with the steel while both the sample and the steel were heated to 400 F.

Detailed data for all experimental work in the high-pressure equipment are given in the Appendix, Tables A-2, A-3, and A-4.

Results and Discussion

In the studies at 1 atmosphere hydrogen pressure it was necessary to vacuum anneal the samples to dissolve surface oxide before exposure to hydrogen to initiate a reaction. Consequently, the first few experimental runs using the pressure balance were done with a vacuum anneal before the addition of hydrogen. These runs are summarized in Table 5. It was found that the samples were oxidized at the 1500 F vacuum annealing temperature and failed to react with hydrogen. Apparently the vacuum was not high enough to prevent contamination of the surface at that temperature. In an attempt to improve the vacuum, a 2-mil sheet of unabraded titanium foil was used to line the inside of the reaction tube. The foil acted as a getter and Sample 4 did react heavily with hydrogen. Sample 5, which was exposed in a foil-lined chamber after a longer anneal, reacted catastrophically. One additional run was made with a lower temperature vacuum anneal and a reaction occurred (Sample 7), but, since a previous run (Sample 6, Table 7) had proved that vacuum annealing was unnecessary to initiate a reaction at a hydrogen pressure of 300 psig (21 atmospheres) if the sample was abraded before exposure to hydrogen, it was decided to eliminate the vacuum annealing treatment.

A series of experimental runs was made with Ti-50A samples cleaned only by degreasing before hydrogen exposure. The results are shown in Table 6. No reaction

TABLE 5. EFFECT OF VACUUM ANNEALING Ti-50A PRIOR TO EXPOSURE TO HYDROGEN AT GREATER THAN ATMOSPHERIC PRESSURE

Hydrogen Exposure			Vacuum Annealing		Description of Results	Sample No. (a)
Temp, F	Pressure, psig	Time, hours	Time, hours	Temp, F		
250	172	18	2-1/2	1500	Sample oxidized, no hydride found.	1
200	156	62	2	1500	Sample oxidized but hydriding ^(c) occurred in one small area.	2
250	300	17	2-1/4	1500	Sample oxidized, no hydride found.	3
180	324	64	2	1500	Heavily hydrided.	4 ^(b)
130	316	--	23	1500	Catastrophic reaction occurred.	5 ^(b)
100	292	23-1/3	13	1000	Thin discontinuous hydride.	7

(a) Complete data are given in Appendix Table A-2.

(b) A titanium foil (Ti-65A) lining was placed inside the reaction tube to act as a getter to provide a better vacuum during annealing.

(c) Oxygen analysis, 3300 ppm.

TABLE 6. THE EFFECT OF THE REACTION OF HYDROGEN ON UNABRADED Ti-50A
SAMPLES AT GREATER THAN ATMOSPHERIC PRESSURE

Hydrogen Exposure			Description of Results	Analysis, H ₂ ppm	Sample No. (a)
Temp, F	Pressure, psig	Time, hours			
75	1000	6-1/3	No hydride found.	--	12
99	1000	6	No hydride found.	35	13
99	305	30-1/2	No hydride found.	33	20
137	307	7-1/2	No hydride found.	--	21
99	295	2-1/3	Thinly hydrided under oxide coating on one end.	--	11 ^(b)

(a) Complete data are given in Appendix Table A-2.

(b) Sample had been oxidized 36 hours at 1150 F before exposure to hydrogen.
Oxide thickness 57 microinches.

occurred in any run at temperatures from 75 to 137 F and pressures from 300 (21 atmospheres) to 1000 psig (69 atmospheres). One sample (Sample 11) had been previously oxidized 36 hours at 1150 F and had a 57-microinch oxide layer covering its surfaces. It reacted with hydrogen in one region under the oxide layer causing some of the oxide to spall. This result was unexpected, and no reason for the observed behavior was apparent. It is possible that in handling the sample prior to hydrogen exposure a small scratch or defect was introduced into the oxide coating which exposed a clean titanium surface to the hydrogen, thus initiating a reaction.

A number of experimental runs were made using samples abraded immediately before exposure to hydrogen to determine the range of pressures over which the Ti-50A-hydrogen reaction would take place and to attempt to correlate hydride-layer thickness with hydrogen pressure. These are shown in Table 7. Pressures ranged from 2 psig (1+ atmosphere) to 1005 psig (69.5 atmospheres). A hydrogen reaction occurred at all pressures except 2 psig (1+ atmosphere). In the work using the glass system at 1 atmosphere hydrogen pressure, a titanium-hydrogen reaction occurred at room temperature if the sample was both abraded and vacuum annealed before hydrogen exposure; in the studies summarized in Table 7 reaction occurred at all pressures at or above 20 psig (2.4 atmospheres) when samples were abraded before exposure. Therefore, it can be concluded that at some pressure between 20 and 2 psig (2.3 to 1+ atmospheres) it becomes necessary to vacuum anneal a titanium sample to cause a titanium-hydrogen reaction to take place at room temperature.

A definite correlation of hydrogen pressure with hydride-layer thickness was obtained as shown in Figure 9. Below a pressure of 300 psig (21.4 atmospheres) the hydride layer became discontinuous and irregular, and correlation with hydrogen pressure was not feasible.

As mentioned previously, thermal instability of the pressure balance precluded determination of hydride reaction kinetics. Even if the pressure balance had allowed reliable readings of weight change as a function of time, the discontinuous and irregular nature of the hydride that formed on most samples would probably have prevented a meaningful analysis of reaction kinetics, as it is unlikely that a single rate-controlling mechanism was operative for the majority of the runs. Data shown in Table 7 for Samples 8 and 25, similarly exposed at 300 psig for 75 and 96 hours, suggest linear kinetics. However, in view of undemonstrated reproducibility and the irregular nature of hydriding during short exposure, this indication is highly questionable.

Sample 26 was abraded and then exposed to air for 24 hours before exposure to hydrogen. A few isolated spots of hydride were found and confirmed by a hydrogen analysis of 51 ppm. To investigate more fully this effect of exposure to air after abrasion and before hydrogen exposure, a series of four experimental runs was made on Ti-50A and Ti-6Al-4V as described in the Experimental Methods Section and summarized in Table 8. It was found that as length of time in air after abrasion increased, the extent of reaction with hydrogen decreased in samples of Ti-50A with all three grain structures. The extent of hydriding on the acicular Ti-50A is shown in Figure 10. Very little hydride was found on the acicular or cold-rolled Ti-50A after 4 hours of air exposure, prior to hydrogen exposure, and none was found on the equiaxed material. All five samples having the acicular structure reacted with hydrogen to a greater extent than did any samples having the cold-rolled or equiaxed structures. Little difference was noted in the reactivities of the cold-rolled and equiaxed Ti-50A material except for the failure of the

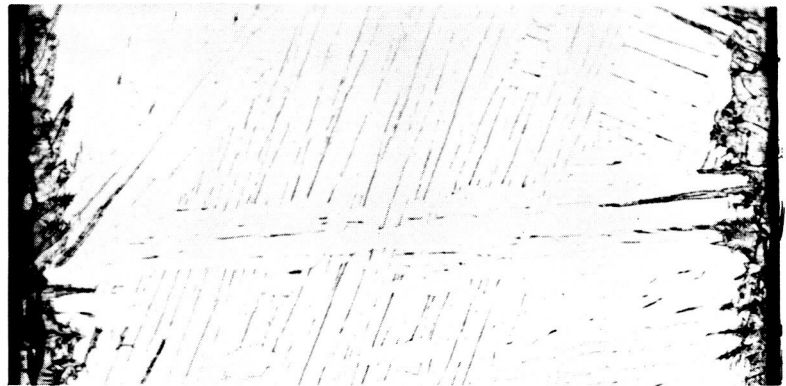
TABLE 7. THE EFFECT OF PRESSURE ON THE REACTION OF Ti-50A WITH HYDROGEN
(All samples abraded before exposure)

Hydrogen Exposure			Description of Hydride	Analysis, H ₂ ppm	Sample No. (a)
Temp, F	Pressure, psig	Time, hours			
75-90	300	30-1/2	Thin continuous; some deep penetration.		24
"	"	72	Thin discontinuous.		23
"	"	96-1/4	Thin discontinuous	365	6
95-105	2	79	No hydride found.	40	22
"	20	76-1/4	Thinly hydrided in isolated areas.	97	19
"	70	29	Thin discontinuous.		18
"	130	6-1/2	Thin discontinuous.		15,17
"	300	6	Thin discontinuous.		16
"	"	75	Thin continuous, 0.00037 inch		8
"	"	96	Thin continuous, 0.00049 inch.		25
"	"	96	A few isolated spots.	51	26 ^(b)
"	590	24	Thin discontinuous.		9
"	"	95	Heavy continuous, 0.00061 inch.		10
"	1000	76-1/2	Heavy continuous, 0.00073 inch.		14

(a) Complete data are given in Appendix Table A-2.

(b) Sample exposed to air 24 hours after abrading and before exposure to hydrogen.

- a. Reacted in 1005 psig (69.5 atmospheres) hydrogen pressure for 76-1/2 hours, average hydride thickness 0.00073 inch. (Note deep penetration)



250X

8B558

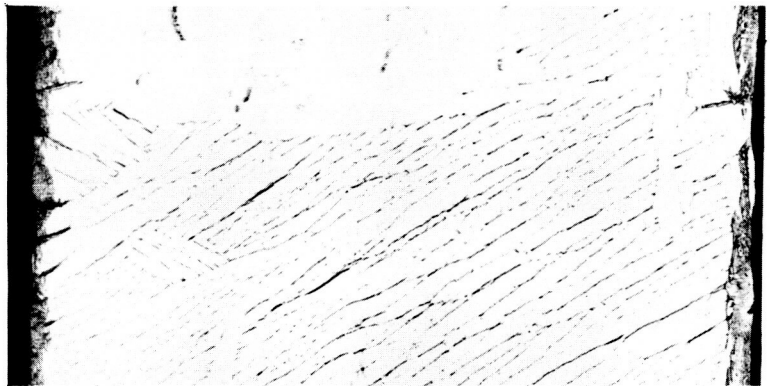
- b. Reacted in 585 psig (40.8 atmospheres) hydrogen pressure for 95 hours, average hydride thickness 0.00061 inch.



250X

8B559

- c. Reacted in 307 psig (21.9 atmospheres) hydrogen pressure for 96 hours, average hydride thickness 0.00049 inch.



250X

8B560

FIGURE 9. THE EFFECT OF HYDROGEN PRESSURE ON HYDRIDE-LAYER THICKNESS

All three samples were acicular Ti-50A and were reacted at 99 F.

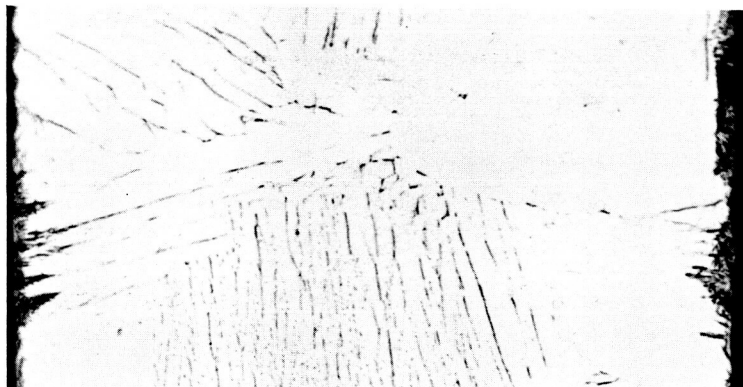
TABLE 8. THE EFFECT OF EXPOSURE TO AIR AFTER ABRASION AND BEFORE EXPOSURE TO 311 PSIG (22.1 ATMOSPHERES) HYDROGEN FOR 24 HOURS AT 99 F^(a)

Time in Air	Description of Hydride
<u>Acicular Ti-50A</u>	
5 min	Thin discontinuous hydride layer.
15 min	Thin discontinuous hydride layer.
1 hr	Thin hydride layer in isolated areas.
2 hr	Thin hydride layer in isolated areas. Less than 1-hr sample.
4 hr	Isolated spots of hydride. Less than 2-hr sample.
<u>Cold Rolled Ti-50A</u>	
5 min	Thin hydride layer in isolated spots.
15 min	Thin hydride layer in isolated spots. Less than 5-min sample.
1 hr	A few isolated spots of hydride.
2 hr	A few isolated spots of hydride. Less than 1-hr sample.
4 hr	A very few isolated spots of hydride. Less than 2-hr sample.
<u>Equiaxed Ti-50A</u>	
5 min	Thin discontinuous hydride layer.
15 min	Thin hydride layer in isolated areas.
1 hr	Thin hydride layer in isolated areas. Less than 15-min sample.
2 hr	A few isolated spots of hydride.
4 hr	No hydride found.
<u>Acicular Ti-6Al-4V</u>	
5 min	No hydride found. Hydrogen analysis 114 ± 1 ppm. ^(b)
15 min	No hydride found.
1 hr	No hydride found.
2 hr	No hydride found.
4 hr	No hydride found.

(a) Complete data are given in Appendix Table A-3.

(b) Base analysis 70 ppm hydrogen.

- a. Exposed to air 5 min
after abrading and
before exposure to
hydrogen



250X

8B549

- b. Exposed to air 1 hour
after abrading and
before exposure to
hydrogen



250X

8B550

- c. Exposed to air 4 hours
after abrading and
before exposure to
hydrogen



250X

8B551

FIGURE 10. THE EFFECT OF EXPOSURE TO AIR AFTER ABRADING AND
PRIOR TO EXPOSURE TO HYDROGEN

All three samples were acicular Ti-50A and were reacted with
311 psig (22.1 atmospheres) hydrogen for 24 hours at 99 F.

equiaxed sample to react with hydrogen after 4 hours of air exposure. It is apparent from these observations that acicular Ti-50A is the least affected by exposure to air after abrading, or is most reactive with hydrogen, and that equiaxed Ti-50A is the most affected by exposure to air, or the least reactive with hydrogen.

The samples of acicular Ti-6Al-4V showed no hydride in metallographic examination indicating a level of hydrogen content below 500 ppm. Vacuum fusion hydrogen analysis showed only 114 ppm present in the sample exposed 5 minutes to air before hydrogen exposure. The base analysis was 70 ppm hydrogen. Consequently, it can be assumed that very little reaction with hydrogen occurred with the longer exposures to air after abrasion and that acicular Ti-6Al-4V was more resistant to hydriding after exposure to air than any of the other materials used in this work.

The application of stress to the samples in 1 atmosphere hydrogen pressure proved to be ineffective in initiating a hydriding reaction. To examine the effect of stress at a hydrogen pressure of 312 psig (22.3 atmospheres) hydrogen, three experimental runs were made as described in the Experimental Methods Section and shown in Table 9. No evidence of hydriding was found on any sample which had not been abraded prior to stressing and hydrogen exposure. The samples which had been abraded prior to stressing and hydrogen exposure did not show a heavier concentration of hydride in the strained area. Acicular Ti-50A again showed the greatest hydride reaction with a thin discontinuous layer over the entire surface, while the cold-rolled and equiaxed material showed hydride in isolated spots. No hydride was found microscopically on the acicular Ti-6Al-4V sample; however, vacuum fusion analysis showed 92 ppm hydrogen, a slight increase over the base analysis of 70 ppm. The Ti-50A samples which had been re-abraded only in the stressed area just before sealing into the reaction system showed a thin continuous hydride layer in that area for all three grain structures. The hydride layer formed on the acicular Ti-50A is shown in Figure 11. The remainder of the surface of the acicular material contained a thin discontinuous hydride layer while the cold-rolled and equiaxed material contained isolated spots of hydride outside the strained area.

Several isolated areas of hydride were found on the inner surface of the stressed and reabraded equiaxed material at some distance from the strained area. These hydrided areas differed considerably from those found on all Ti-50A samples previously exposed to hydrogen and on other areas of the same sample. This hydride, rather than being all concentrated near the surface, appeared to radiate inward in small needlelike particles from the surface hydrided areas as shown in Figure 12. Apparently, the surface was rubbed or slightly scratched in this area by the steel die used in bending the sample. This probably initiated the reaction, which perhaps caused local heating in spots, resulting in an inward diffusion of the hydride from the surface hydrided areas.

Data from the four experimental runs made with the Beech Aircraft titanium tubing are presented in the Appendix, Table A-2, Samples 27 through 30. Figure 13 shows the hydride formed on the inner wall only, of the tubing exposed to 315 psig (22.4 atmospheres) of hydrogen for 24 hours at 99 F. This tubing was exposed in the as-received condition, with no pretreatment except degreasing in cp acetone. The tubing after etching and exposure to hydrogen is shown in Figure 14. No reaction with hydrogen occurred. Figures 15 and 16 show the hydride formed on the inside surface of the titanium tubing after rubbing this surface with a piece of high-carbon, high-chromium steel to simulate what is believed to take place during fabrication of the tubing. Note the similarity of this hydride to that found on the equiaxed material which was believed to have

TABLE 9. THE EFFECT OF A STATIC STRESS NEAR THE YIELD STRESS ON THE REACTION OF TITANIUM WITH 312 PSIG (22.2 ATMOSPHERES) HYDROGEN FOR 24 HOURS AT 99 F^(a)

Material	Description of Hydride
<u>Not Abraded</u>	
Acicular Ti-50A	No hydride found.
Cold Rolled Ti-50A	No hydride found.
Equiaxed Ti-50A	No hydride found.
Acicular Ti-6Al-4V	No hydride found.
<u>Abraded</u>	
Acicular Ti-50A	Thin discontinuous hydride layer. Not concentrated in strained area.
Cold Rolled Ti-50A	Scattered spots of hydride. Not concentrated in strained area. More appear to be near ends of sample.
Equiaxed Ti-50A	More hydride than in cold rolled sample. Not concentrated in strained area. More appear to be near ends of sample.
Acicular Ti-6Al-4V	Hydrogen analysis 92 ± 2 ppm. ^(b)
<u>Re-abraded in Strained Area</u>	
Acicular Ti-50A	Thin continuous hydride layer in re-abraded area; discontinuous elsewhere.
Cold Rolled Ti-50A	Thin continuous hydride layer in re-abraded area; spotty hydrided areas elsewhere.
Equiaxed Ti-50A	Thin continuous hydride layer in re-abraded areas. One leg contained heavy spots of hydride with needle-like particles extending inward 1/3 to 1/2 sample thickness.
Acicular Ti-6Al-4V	No hydride found.

(a) Complete data are given in Appendix Table A-4.

(b) Base analysis 70 ppm hydrogen.

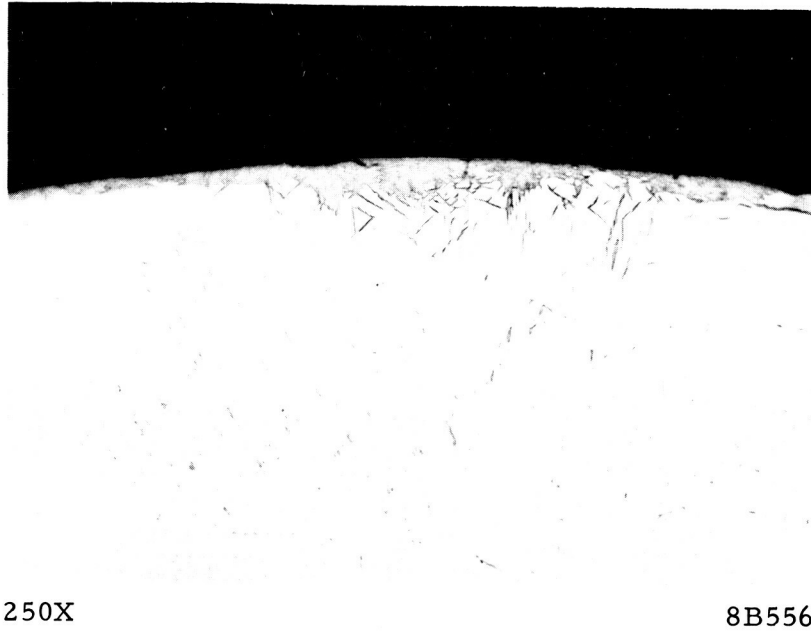


FIGURE 11. HYDRIDE ON STRESSED AREA OF ACICULAR Ti-50A SAMPLE

Sample reabraded in this stressed area before exposure to 312 psig (22.2 atmospheres) hydrogen for 24 hours at 99 F.

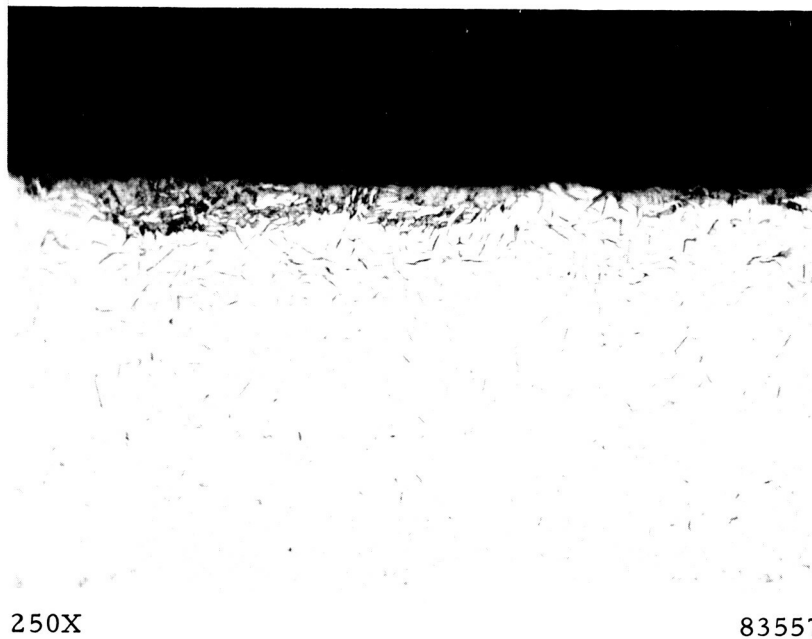
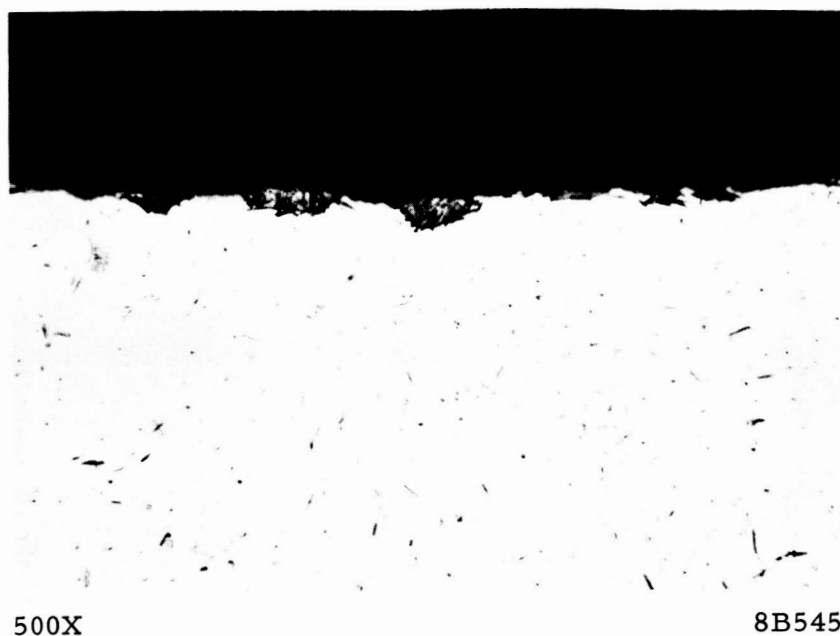


FIGURE 12. HYDRIDE ON EQUIAXED Ti-50A SAMPLE

Same run as above sample but not stressed or reabraded in this area. Believed to have been scratched by dies during bending. Note similarity to Figures 15 and 16.



500X

8B545

FIGURE 13. HYDRIDE AREAS ON INSIDE OF TITANIUM TUBING SAMPLE 27

Reacted in the "as-received" condition with 315 psig (2.24 atmospheres) hydrogen for 24 hours at 99 F.



500X

8B546

FIGURE 14. SURFACE OF INSIDE OF TITANIUM TUBING WHICH WAS ETCHED AND DID NOT HYDRIDE, SAMPLE 28

Tube etched in HNO_3 -HF- H_2O solution, then exposed to 311 psig (22.2 atmospheres) hydrogen for 24 hours at 99 F.

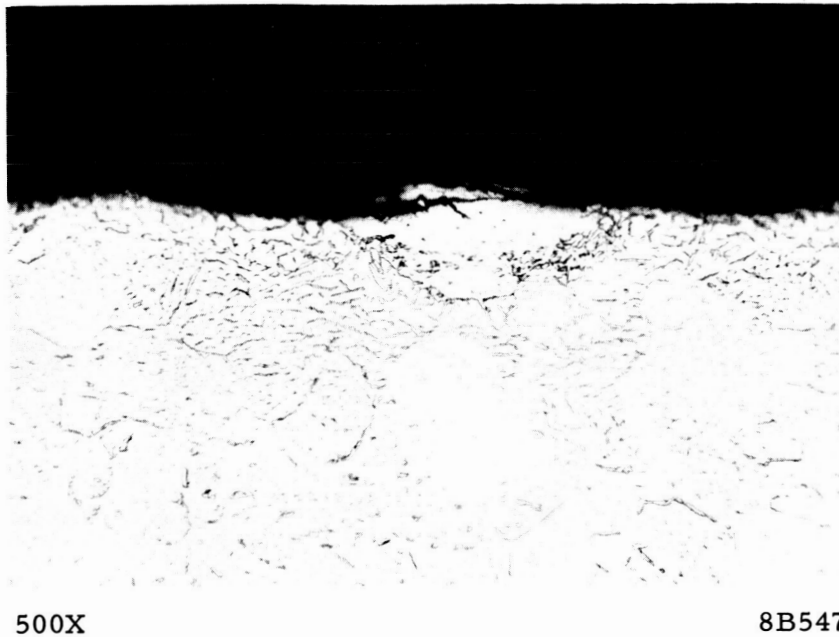


FIGURE 15. HYDRIDED AREA ON INSIDE OF TITANIUM TUBING SAMPLE 29

Rubbed with steel before reacting with 313 psig (22.3 atmospheres) hydrogen at 99 F for 24 hours. Note radiating hydride particles. Large particles 1.4 mils thick. Radiating particles extend to over 1/3 of tube-wall thickness.



FIGURE 16. A REPRESENTATIVE AREA OF HYDRIDE FORMED ON INSIDE OF TITANIUM TUBING SAMPLE 29

Another area of the above sample, showing penetration of the hydride particles. Note similarity to Figure 12.

been scratched by steel during stressing (Figure 12). A fourth piece of tubing was rubbed with the same steel while both were heated in air at 400 F. No increase in hydriding above that found on the as-received material occurred. This was probably due to the increase in oxidation of the surface caused by heating in air.

GENERAL DISCUSSION

Those specimens that were reacted in the glass system under 1 atmosphere hydrogen pressure required vacuum annealing before hydrogen exposure, and often the presence of a titanium foil getter to produce a reaction. Apparently, a pressure between about 2 psig (1.1 atmospheres) and 20 psig (2.4 atmospheres) eliminates the need for vacuum annealing of the specimens before hydrogen exposure to insure a reaction, as shown by studies in the high-pressure equipment. However, abrasion of the surface prior to exposure to high-pressure hydrogen was required. The reactivity of the freshly abraded surface decreased considerably when exposed to air for a few hours. Pressure also directly affects the thickness of the hydride layer formed. These observations are valid only for clean systems and high-purity, dry hydrogen. The importance of system and gas cleanliness is shown by the previous work in a less clean system in which few reactions took place at high pressure even with abraded and vacuum-annealed specimens exposed to hydrogen at temperatures to 300 F.⁽¹⁾ Cyclic stressing at 1 atmosphere pressure or static stressing at higher pressures seemed to have had no effect on the titanium-hydrogen reaction under the conditions of the runs made in this work. Resistivity was not increased under conditions where reaction normally occurred, nor was reactivity induced under conditions which did not lead to reaction in unstressed samples. It is not known whether the Ti-6Al-4V alloy specimen which did react during cyclic stressing would perhaps have reacted without any stress having been applied.

The effect of a range of temperature on the titanium-hydrogen reaction was not investigated. It is known that a reaction will occur with a properly prepared sample at a temperature as low as 78 F, regardless of pressure. However, if a reaction is not initiated at a temperature in this range, it was found that none would occur up to 250 F at atmospheric hydrogen pressure. Once a reaction has been initiated, it will proceed at a greater rate with increase in temperature. Unfortunately, this change in rate with temperature could not be investigated because of the instability of the pressure balance.

The microstructure of Ti-50A was found to affect the extent of the titanium-hydrogen reaction at pressures above atmospheric. The acicular structure was most reactive and the least affected by exposure to air after abrasion and prior to exposure to hydrogen. There was little difference in the reactivity of the cold-rolled and equiaxed material except that a slight reaction with hydrogen had still occurred after 4 hours of exposure to air after abrading with the cold-rolled material but not with the equiaxed material. The acicular Ti-6Al-4V material appeared to be the least reactive of all material examined at hydrogen pressures above atmospheric, but it was the only one to hydride under stress in the glass system. Further study of this alloy would be necessary before a definite conclusion could be drawn concerning its reactivity compared to Ti-50A.

The results obtained using the Ti-55A titanium tubing are believed to be quite significant. No reaction with hydrogen had occurred at any pressure, and with any of the three grain structures of Ti-50A, unless it had been abraded prior to hydrogen exposure. The tubing material reacted with no special surface preparation. A light acid pickle prevented reaction, and galling of the surface with an iron alloy increased it. Apparently, the hydriding reaction is activated by some form of surface contamination. It seems most likely that the activating agent is iron contamination from the mandrel used in tube drawing. If so, contamination from machining, forging, or forming operations might also be anticipated. Of special note is that present results suggest that the contamination can be rather easily eliminated by acid pickling.

FUTURE WORK

The studies described in this report show that a freshly abraded titanium surface will react with high-purity hydrogen at ambient temperatures and pressures as low as 20 psig. Also, they suggest that some form of surface contamination, presumably iron contamination, allows the reaction to proceed without prior surface preparation. It is recommended that the present work be continued with emphasis in two areas:

- (1) The effects of contamination on the hydriding reaction, sources of contamination, and treatments to eliminate contamination.
- (2) The effect of mild surface abrasion in a hydrogen atmosphere, of the type which might occur between adjacent titanium components of a vibrating structure, on the hydriding reaction.

It appears fairly certain that one, or possibly both, of these factors was primarily responsible for tank failures observed in service. During studies designed to define the importance of these two factors, it would also be possible to gain additional data relative to the kinetics of the reaction and on the relative susceptibility of different titanium alloys.

* * * * *

The above work is based on data recorded in Battelle Memorial Institute Laboratory Books Nos. 23491 (pp 66-100), 24339 (pp 1-9), and 24281 (pp 1-67).

REFERENCES

- (1) Koehl, B. G., Hodge, W., and Williams, D. N., "An Investigation of the Reaction of Titanium with Hydrogen", Summary Report to NASA, Manned Spacecraft Center, Contract No. NAS 9-5298 (July 14, 1966).
- (2) Williams, D. N., and Maykuth, D. J., "Reaction of Titanium with Gaseous Hydrogen at Ambient Temperature", DMIC Technical Note (February 4, 1966).

APPENDIX

EXPERIMENTAL RESULTS

A-1

TABLE A-1. SUMMARY OF STRESS HYDRIDING EXPERIMENTS IN GLASS APPARATUS

Sample or Run	Sample Treatment	Foil Treatment	Type of Sample	Oxide Thickness, microinch	Time, hours	H ₂ Absorbed, ml	Remarks
				<u>Unstrained</u>			
TR-1	Annealed	Annealed	Acicular Ti-50A	--	17-1/2	170	35-mil material used to test equipment. Continuous hydride layer of medium thickness on sample and foil.
TR-2	Annealed	Annealed	Acicular Ti-50A	--	20	153	15-mil material used and will be used for all further runs. Heavy, continuous hydride layer on sample, thin discontinuous layer on foil.
TR-3	Annealed	Annealed	Acicular Ti-50A	--	63-1/2	434	Sample holder used to hold sample. Not stressed. Heavy continuous hydride layer on sample and foil.
TR-4	Not annealed	No foil used	Acicular Ti-50A	--	20	None	No hydride found.
				<u>Strained 0.3 Percent in Bending</u>			
1-S	Not annealed, stressed	No foil used	Acicular Ti-50A	--	26-1/2	None	One very small spot of hydride found on sample.
2-S	Annealed, stressed	Annealed	Acicular Ti-50A	--	17-1/2	590	Continuous hydride layer on sample and foil. Not as heavy as TR-3 which was not stressed.
3-S	Not annealed, stressed	No foil used	Acicular Ti-50A	--	23-1/2	None	No hydride found.
4	Not annealed	Annealed	Acicular Ti-50A	--	65	None	System leak occurred.
5-S	Not annealed, stressed	Annealed	Acicular Ti-50A	--	24	386	No hydride found on sample. Foil heavily hydrided.
6-0-S	Not annealed, stressed, oxidized	Annealed	Acicular Ti-50A	15	17	385	No hydride found on sample. Foil heavily hydrided.
7-0-S	Not annealed, stressed, oxidized	Annealed	Acicular Ti-50A	22	17-1/2	329	No hydride found on sample. Foil heavily hydrided.
8-0-S	Not annealed, stressed, oxidized	Annealed	Acicular Ti-50A	28	17-1/2	242	No hydride found on sample. Foil heavily hydrided.
9-0-S	Not annealed, stressed, oxidized	Annealed	Equiaxed Ti-50A	12	85-1/2	303	16-1/2 hours at 80 F, 69 hours at 140 F. No hydride found on sample. Foil heavily hydrided.

TABLE A-1. (Continued)

Sample or Run	Sample Treatment	Foil Treatment	Type of Sample	Oxide Thickness, microinch	Time, hours	H ₂ Absorbed, ml	Remarks
10-0-S	Not annealed, stressed, oxidized	Annealed	Acicular Ti-50A	20	17	None	Run made at 140 F. No hydride found on sample or foil.
11-S	Not annealed, stressed	Annealed	Acicular Ti-50A	--	17	294	No hydride found on sample. Foil heavily hydrided.
12-S	Not annealed, stressed	Annealed	Acicular Ti-50A	--	65-1/2	17	Stress applied in one direction only. No hydride found on sample, only light hydride on foil.
13-S	Not annealed, stressed	Annealed	Acicular Ti-50A	--	17-1/2	None	Run made at 250 F. No hydride formed on sample or foil.
14-0-S	Not annealed, stressed, oxidized	Annealed	Acicular Ti-50A	75	17-1/2	None	Run made at 140 F. No hydride found on sample or foil. White outer oxide layer had cracked but inner bronze layer had not.
15-0-S	Not annealed, stressed, oxidized	Annealed	Acicular Ti-50A	75	67	None	No hydride found on sample or foil. White outer oxide layer had cracked but inner bronze layer had not.
16-S	Not annealed, stressed	Annealed	Acicular Ti-6Al-4V	--	138	650	Sample and foil both hydrided.
17-S	Not annealed, stressed	No foil used	Acicular Ti-6Al-4V	--	21	None	No indication of hydriding.
18-S	Not annealed, stressed	Annealed	Acicular Ti-50A	--	42-1/2	470	No hydride found on sample. Foil hydrided.
19-S	Not annealed, stressed	No foil used	Acicular Ti-50A	--	94	None	No hydride found on sample.
<u>Strained 1.0 Percent in Bending</u>							
20-0-S	Not annealed, stressed, oxidized	No foil used	Acicular Ti-50A	75	19	None	2 hours at 80 F and 17 hours at 140 F. Sample broke from stress but did not hydride.
21-0-S	Not annealed, stressed, oxidized	No foil used	Acicular Ti-50A	149	18-1/2	None	2 hours at 80 F, 16-1/2 hours at 140 F. No hydride found on sample. White outer oxide layer cracked, inner bronze layer did not.
22-S	Not abraded or annealed, stressed	Annealed	Acicular Ti-50A	--	66	25	No hydride found on sample. Foil hydrided slightly.

TABLE A-1. (Continued)

Sample or Run	Sample Treatment	Foil Treatment	Type of Sample	Oxide Thickness, microinch	Time, hours	H ₂ Absorbed, ml	Remarks
23-0-S	Not annealed, stressed, oxidized	No foil used	Equiaxed Ti-50A	11	19	None	Did not crack outer oxide layer. No hydride found on sample.
24-S	Not annealed, stressed	No foil used	Acicular Ti-50A	--	116	None	21 hours at 80 F, 27 hours at 170 F, and 68 hours at 80 F. Sample broke from stress during 170 F period. No hydride found on sample.
25-S	Not abraded or annealed, stressed	No foil used	Acicular Ti-6Al-4V	--	237	None	Sample did not break but several microscopic cracks were visible after over 14,000 stress cycles. No indication of hydriding.
26-S	Not annealed, stressed, oxidized	No foil used	Acicular Ti-50A	57	283	None	115 hours at 80 F, 168 hours at 140 F. Sample broke from stress after first 20 hours. No hydride found on sample.
27-S	Not annealed, stressed, scratched with Fe	No foil used	Acicular Ti-50A	--	379	None	Sample broke from stress after 20 hours. No hydride found on sample.

Note: Samples 1 through 19 were stressed on a mandrel with 2.54-inch radius, while Samples 20 through 27 were stressed on a mandrel having a 0.75-inch radius.

All runs made at room temperature of 80 F unless stated otherwise.

TABLE A-2. SUMMARY OF EXPERIMENTAL RUNS MADE AT ABOVE ATMOSPHERIC PRESSURE
USING QUARTZ-SPRING BALANCE

Sample or Run	Temp., F	Pressure, psig	Reaction Time, hours	H ₂ Absorbed		Remarks
				From Analytical Balance, mg	Calc. from Spring Change, mg	
MB-1	250	172	18	--	--	Annealed 2-1/2 hours at 1500 F before H ₂ addition. Sample oxidized, no hydride formed.
-2	200	156	62	--	--	Annealed 2 hours at 1500 F before H ₂ addition. Sample oxidized but hydriding occurred in one small area. Analysis shows 3300 ppm O ₂ , 24 ppm H ₂ .
-3	250	300	17	--	--	Annealed 2-1/4 hours at 1500 F before H ₂ addition. Sample oxidized, no hydride formed.
-4(a)	180	324	64	--	--	Annealed 2 hours at 1500 F before H ₂ addition. Sample heavily hydrided.
-5(a)	130	316	--	--	--	Annealed 23 hours at 1500 F before H ₂ addition. A catastrophic reaction occurred with both the sample and titanium foil getter reacting.
-6	90	300	96-1/4	1.2	0.9	Thin, discontinuous hydride layer. Analysis shows 365 ppm H ₂ .
-7	100	292	23-1/2	0.7	1.5	Annealed 13 hours at 1000 F before H ₂ addition. Thin discontinuous hydride layer.
-8	96	297	75	0.8	3.8	Thin continuous hydride layer 0.00037 inch in thickness.
-9	98	593	24	0.5	1.9	Thin discontinuous hydride layer.
-10	99	585	95	2.1	3.5	Heavy continuous hydride layer 0.00061 inch in thickness.
-11	99	295	2-1/3	--	--	Oxidized 36 hours at 1150 F before H ₂ addition. Hydrided under oxide layer on one end of sample causing some oxide to spall off.
-12	75	1000	6-1/3	-0.3	0.4	Not abraded. No hydride found on sample.
-13	99	1000	6	-0.1	1.3	Not abraded. No hydride found on sample except for a small area around suspension hole. The abrasive action of drilling hole removed oxide and presented a clean surface for attack by H ₂ . Analysis, 35 ppm H ₂ .
-14	99	1005	76-1/2	1.1	2.5	Heavy continuous hydride layer 0.00073 inch in thickness. Deep penetration in some areas.
-15	99	125	6	0.3	1.6	Thin, discontinuous hydride layer concentrated near one end.

TABLE A-2. (Continued)

Sample or Run	Temp., F	Pressure, psig	Reaction Time, hours	H ₂ Absorbed		Remarks
				From Analytical Balance, mg	Calc. from Spring Change, mg	
-16	99	306	6	0.2	2.0	Thin, discontinuous hydride layer over most of surface. Deeper penetration at one end.
-17	99	130	7	0.3	1.2	Thin, discontinuous hydride layer concentrated at one end.
-18	99	67	29	0.1	0.6	Thin, discontinuous hydride layer over entire surface.
-19	99	20	76-1/4	0.2	0.5	Thinly hydrided in isolated spots. Analysis, 97 ppm.
-20	99	305	30-1/2	-0.3	0.4	Not abraded. No hydride found on specimen except a small area around suspension hole. Analysis 33 ppm H ₂ .
-21	137	307	7-1/2	-0.1	0.5	Not abraded. No hydride found on specimen except a small area around suspension hole.
-22	99	2	79	-0.2	0.7	No hydride found on specimen. Analysis, 40 ppm H ₂ .
-23	87	304	72	0.0	0.4	Heated by hot H ₂ O on coils of system. No furnace. Thin, discontinuous hydride layer concentration near one end.
-24	78	306	30-1/2	0.6	0.6	No heating of any kind. Entire system at room temperature. Thin, continuous hydride layer. Some deep penetration at one end.
-25	99	307	96	0.7	2.7	Thin, continuous hydride layer, 0.00049 inch in thickness.
-26	99	309	96	0.0	1.0	Sample abraded, then exposed to air 24 hours before H ₂ addition. A few, very small, irregular spots of hydride found on specimen. Analysis shows 51 ppm H ₂ .
-27	99	315	24	-0.1	0.8	Beech Ti tube. Not abraded. Isolated spots of hydride found on inside of tube.
-28	99	311	24	-0.2	0.7	Beech Ti tube. Etched in HNO ₃ -HF-H ₂ O. No hydride found on sample.
-29	99	313	24	-0.1	0.5	Beech Ti tube. Inside rubbed with H-11 steel at room temperature. Much more hydride formed than in Run 27. Needlelike hydride particles radiated from surface hydride to penetrate almost half sample thickness.
-30	99	312	24	0.0	(b)	Beech Ti tube. Inside rubbed with H-11 steel at 400 F. Hydride found but no greater quantity than that formed on the as-received material.

- (a) A titanium foil (Ti-65A) lining was placed inside reaction tube to act as a getter to insure a better vacuum during annealing.
 (b) Quartz spring not used because of the small size of the sample.

TABLE A-3. SUMMARY OF EXPERIMENTAL RUNS ILLUSTRATING THE EFFECT OF SAMPLE EXPOSURE TO AIR ON THE TITANIUM-HYDROGEN REACTION AT GREATER THAN ATMOSPHERIC PRESSURE

Run	Sample	Temp., F	Pressure, psig	Time in Air	Sample Weight		Gain or Loss, mg	Description of Hydride
					Before, g	After, g		
<u>Acicular Ti-50A</u>								
P-1	A	99	311	5 min	0.8608	0.8612	+0.4	Thin, discontinuous hydride layer.
	B	"	"	15 min	0.9094	0.9098	+0.4	Thin, discontinuous hydride layer.
	C	"	"	1 hr	1.0241	1.0244	+0.3	Thin layer in isolated areas.
	D	"	"	2 hr	1.0302	1.0302	0.0	Thin layer in isolated areas. Less than Sample C
	E	"	"	4 hr	0.9955	0.9953	-0.2	Isolated spots of hydride. Less than Sample D.
<u>Cold-Rolled Ti-50A</u>								
P-2	A	99	312	5 min	0.8283	0.8284	+0.1	Thin hydride layer in isolated spots.
	B	"	"	15 min	0.8508	0.8507	-0.1	Thin hydride layer in isolated spots. Less than Sample A.
	C	"	"	1 hr	0.8459	0.8457	-0.2	A few isolates spots of hydride.
	D	"	"	2 hr	0.8476	0.8475	-0.1	A few isolated spots of hydride. Less than Sample C.
	E	"	"	4 hr	0.8839	0.8838	-0.1	A few isolated spots of hydride. Less than Sample D.
<u>Equiaxed Ti-50A</u>								
P-3	A	99	311	5 min	1.1108	1.1110	+0.2	Thin, discontinuous hydride layer.
	B	"	"	15 min	1.1272	1.1272	0.0	Thin hydride layer in isolated areas.
	C	"	"	1 hr	1.1579	1.1578	-0.1	Thin hydride layer in isolated areas. Less than Sample B.
	D	"	"	2 hr	1.1454	1.1454	0.0	Isolated spots of hydride.
	E	"	"	4 hr	1.1596	1.1596	0.0	No hydride found.
<u>Ti-6Al-4V</u>								
P-4	A	99	311	5 min	1.1710	1.1710	0.0	Hydrogen content 114 ± 1 ppm ^(a) .
	B	"	"	15 min	1.1836	1.1835	-0.1	No hydride found.
	C	"	"	1 hr	1.1832	1.1831	-0.1	No hydride found.
	D	"	"	2 hr	1.1773	1.1771	-0.2	No hydride found.
	E	"	"	4 hr	1.1388	1.1387	-0.1	No hydride found.

Note: All experimental runs were of 24-hour duration.

The sensitivity of the analytical balance is ± 0.2 mg. This accounts for the observing of hydride microscopically though no weight gain is shown by the balance readings.

(a) Base hydrogen analysis was 70 ppm.

A-7 and A-8

TABLE A-4. SUMMARY OF EXPERIMENTAL RUNS ILLUSTRATING THE EFFECT OF STRESS ON THE TITANIUM-HYDROGEN REACTION AT GREATER THAN ATMOSPHERIC PRESSURE

Run	Sample	Temp., F	Pressure, psig	Structure	Sample Weight			Description of Hydride
					Before, g	After, g	Gain or Loss, mg	
<u>Not Abraded</u>								
P-5	A	99	312	A	0.6606	0.6603	-0.3	No hydride found.
	B	"	"	CR	0.6640	0.6637	-0.3	No hydride found.
	C	"	"	E	0.6569	0.6568	-0.1	No hydride found.
	D	"	"	Ti-6Al-4V	0.6340	0.6339	-0.1	No hydride found.
<u>Abraded</u>								
P-6 ^(a)	A	99	312	A	0.6061	0.6060	-0.1	Thin, discontinuous hydride layer. Not concentrated in strain area.
	B	"	"	CR	0.6118	0.6116	-0.2	Scattered spots of hydride, not concentrated in strain area. More appear to be near ends of sample.
	C	"	"	E	0.6166	0.6166	0.0	More hydride than in Sample B but not concentrated in strain area. More appear to be near ends.
	D	"	"	Ti-6Al-4V	0.6676	0.6676	0.0	Hydrogen analysis, 92 ± 2 ppm ^(b) .
<u>Reabraded in Strain Area</u>								
P-7	A	99	312	A	(c)	--	--	Continuous hydride layer in re-abraded area, discontinuous elsewhere.
	B	"	"	CR	--	--	--	Continuous hydride layer in re-abraded area, discontinuous elsewhere.
	C	"	"	E	--	--	--	Continuous hydride layer in re-abraded area. One leg contained spots of heavy hydride with radiating needlelike particles to 1/3 to 1/2 of sample thickness.
	D	"	"	Ti-6Al-4V	--	--	--	No hydride found.

Note: All experimental runs were of 24-hour duration. The sensitivity of the analytical balance is ±0.2 mg. This accounts for the observing of hydride microscopically though no weight gain is shown by the balance readings.

(a) Samples were abraded and degreased. Exposure to air after abrasion, 5 to 10 minutes.

(b) Base hydrogen analysis, 70 ppm.

(c) No weights taken to minimize exposure time to air. Reabraded immediately before sealing to system. Exposure time to air after final abrasion, 2 to 3 minutes.